Standard Operating Procedure for the Analysis of Dissolved-Phase Organic Carbon in Great Lakes Waters

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December 19, 1996

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1.0 Scope and Application

This Procedure describes the analysis of filtrates from Great Lakes water samples for dissolved organic carbon (DOC). After filtration, the analysis of the filtrates is by conversion of organic carbon to CO_2 by an ultraviolet (UV) digester with detection of CO_2 by an infrared (IR) analyzer. This SOP covers standard and instrument preparation, instrument calibration and maintenance, analysis of carbon, and calculation of results.

2.0 Safety and Waste Handling

All applicable safety and waste handing rules are to be followed. These include the proper labeling and disposal of chemical wastes. Over-board discharges of chemical wastes are forbidden. Refer to the GLNPO Safety, Health, and Environmental Compliance Manual for specific rules.

3.0 Summary of Procedure

The determination of organic carbon requires the removal of inorganic carbon, which is present in Great Lakes water samples as carbonate. Removal of inorganic carbon is achieved inside the analyzer by acidifying the sample with 1.0 N sulfuric acid. A high-velocity stream of organic-free air transforms the acidified filtrate into a thin, turbulent liquid film. The film is transported rapidly through a large-bore coil which provides the necessary surface area for efficient CO_2 removal. At a purge rate of 500 mL per minute, up to 500 mg of inorganic carbon can be removed with minimal loss of volatile organic compounds. An aliquot of the carbonate-free filtrate is then segmented in the automatic analyzer for analysis. The aliquot is mixed with a stream of 1.0 N sulfuric acid and potassium persulfate, and subjected to ultraviolet radiation to assure complete oxidation of the organic carbon. The resulting CO_2 is then purged with a stream of CO_2 free air or nitrogen, and is detected with a non-dispersive infra-red analyzer. The signal from the IR detector is output to a strip chart recorder. The concentration of dissolved organic carbon in the filtrate is calculated using the peak height method.

4.0 Description of Instrumentation

The instrumentation consists of a Technicon Auto Analyzer II system, including an Auto Sampler IV, a Proportioning Pump III, a DOC manifold, an ultraviolet digester, and a CO_2 and non-dispersive IR analyzer (Beckman Model 865). A source of CO_2-free air with flow control, indicators, and a strip chart recorder are also used.

5.0 Preparation

5.1 Sample Handling and Preservation

Great Lakes water samples are filtered immediately after collection, transferred to clean glass containers, and stored at 4 °C until analysis. Filtrates are stable for 24 hours if properly stored.

5.2 Interferences

5.2.1 Inorganic carbon is the only known interferant in this analysis. Inorganic carbon is removed in the autoanalyzer through addition of 1.0 N sulfuric acid. Low results for this analysis may be obtained on some volatile organic compounds.

5.2.2 Organic vapors, such as solvents, may contaminate the filtrates unless care is taken.

5.3 Preparation of Reagents

5.3.1 Organic-free, distilled, deionized water (from now on referred to as organic-free water) is used for the preparation of all reagents and standards.

5.3.2 All reagents should be stored in appropriate glass bottles and labeled with reagent identity, date of preparation, concentration, and the initials of the preparer.

5.3.3 1.0 N sulfuric acid reagent: Add 28 mL of concentrated sulfuric acid to about 800 mL of organic-free water. Mix and dilute to one liter.

5.3.4 4% persulfate reagent: Dissolve 40 grams of potassium persulfate ($K_2S_2O_5$) in organic-free water. Mix and dilute to one liter.

5.4 Preparation of Calibration Standards

5.4.1 Stock 1000 mg/L carbon solution: Dissolve 2.125 grams of potassium biphthalate ($KHC_8H_4O_4$) in 500 mL of organic-free water. Add 1 mL of concentrated sulfuric acid (H_2SO_4). Mix and dilute to one liter.

5.4.2 Working calibration standards: Prepare standards to cover the entire range of expected concentrations of DOC. Working calibration standards should be prepared daily . For a typical working range of 0 - 10 mg of carbon/L, the following standards may be used:

mL of stock carbon solution*	Concentration (mg carbon/L)
2.0	10.0
1.0	5.0
0.5	2.5
0.2	1.0
0.1	0.5
0.0	0.0

*diluted to 200 mL in organic-free water.

5.4.3 Stock 514 mg carbon/L control solution: Dissolve 1.2604 grams of glutamic acid ($C_5H_9O_4N$), which has been dried for 2-3 hours at 70°C, in 500 mL of organic-free water. Add 1 mL of concentrated sulfuric acid (H_2SO_4) and dilute to one liter.

5.4.4 Working Control Standards: Prepare the following control standards on a daily basis:

mL of stock control solution*	Concentration (mg carbon/L)
High Check (CS-1) 2.0 mL	5.14
Low Check (CS-2) 0.5 mL	1.28

*diluted to 200 mL in organic-free water.

5.4.5 Label all calibration and control standard solutions with ID, date of preparation, concentration, and initials of the preparer.

6.0 Analytical Procedures

6.1 Instrument Set-up

Assemble the Auto Analyzer DOC manifold following the diagram in Figure 1. Make sure there are no leaks in the air system. Activate the IR detector by turning on the main power switch and allowing it to warm up for a minimum of 2 hours prior to use. At the same time, run CO_2-free air through the IR detector and set the zero control read near zero. After the instrument is assembled and checked against the diagram in Figure 1, switch on the reagent flows, the air flow, the UV digestor and the proportioning pump. Wait for a stable baseline from the IR detector before starting the calibration procedures.

6.2 Procedures

6.2.1 Once a stable baseline from the IR detector has been achieved, run the highest calibration standard (primer). Adjust the strip chart recorder to the appropriate range to keep the peak on the chart paper.

6.2.2 Load the automatic sampler tray and run the remaining calibration standards, check standards, blanks, and Great Lakes water sample filtrates in the following order:

1st: 10 mg carbon/L calibration standard (primer)
2nd: From the 5.0 mg carbon/L standard down to the 0.0 mg carbon/L standard (from high to low)
3rd: a reagent blank
4th: CS-1
5th: CS-2

6th: up to 40 filtrates
7th: a reagent blank
8th: CS-1
9th: CS-2

6.3 Instrument Shut-down

6.3.1 After analysis is completed, some parts of the instrument are shut down. First put the system on wash for at least 30 minutes. Then turn off the automatic sampler, proportioning pump, and UV digestor. The organic-free air supply should be allowed to run through the IR detector.

6.3.2 The infrared detector should be left on.

REPEAT: LEAVE THE IR DETECTOR ON.

7.0 Calculations

Measure the peak heights of the calibration standards (manually). Calculate the regression equation for the calibration curve using a second order regression with zero forcing. Apply this regression equation to determine the DOC concentration in the filtrates from the peak heights.

8.0 Maintenance and Trouble-Shooting

An unstable baseline may indicate that the manifold system may need some tubing replacement or there is a leak in the air system. Change the drierite trap between the phase separator and the IR detector prior to complete exhaustion of the trap.

9.0 Quality Control

9.1 The minimum acceptable correlation coefficient (r) for the calibration curve is 0.995.

9.2 The following criteria are required to be met, with the minimum frequency indicated, for the analysis to be considered in control.

Criterion	Frequency	Limits (mg carbon/L ± 3 std)
High Check (CS-1)	Begin+End, l/40 samples	5.14 ± 0.90
Low Check (CS-2)	Begin+End, 1/40 Samples	1.28 ± 0.60
Reagent Blank	Begin+End, 1/40 Samples	0.00 ± 0.60
Lab. Blank	Begin+End, 1/40 Samples	0.00 ± 0.60

Figure 1.
Dissolved Organic Carbon Manifold Diagram